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**SYMMETRY- AND SOLVENT-DEPENDENT
PHOTOPHYSICS OF FLUORENES CONTAINING
DONOR AND ACCEPTOR GROUPS (POSTPRINT)**

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AFRL/RXAP**

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Interim Report**

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14. ABSTRACT Three two-photon absorption (2PA) dyes (donor– π –donor (DPA2F), donor– π –acceptor (AF240), and acceptor– π –acceptor (BT2F); specifically, D is Ph ₂ N–, A is 2-benzothiazoyl, and the π -linker is 9,9-diethylfluorene) are examined in a variety of aprotic solvents. Because the 2PA cross section is sensitive to the polarity of the local environment, this report examines the solvent-dependent linear photophysics of the dyes, which are important to understand before probing more complex solid-state systems. The symmetrical dyes show little solvent dependence; however, AF240 has significant solvatochromism observed in the fluorescence spectra and lifetimes and also the transient absorption spectra. A 114 nm bathochromic shift is observed in the fluorescence maximum when going from n-hexane to acetonitrile, whereas the lifetimes increase from 1.25 to 3.12 ns. The excited-state dipole moment for AF240 is found to be 20.1 D using the Lippert equation, with smaller values observed for the symmetrical dyes. Additionally, the femtosecond transient absorption (TA) spectra at time zero show little solvent dependence for DPA2F or BT2F, but AF240 shows a 52 nm hypsochromic shift from n-hexane to acetonitrile. Coupled with the solvatochromism in the fluorescence and large excited-state dipole moment, this is attributed to formation of an intramolecular charge-transfer (ICT) state in polar solvents. By 10 ps in AF240, the maximum TA in acetonitrile has shifted 30 nm, providing direct evidence of a solvent-stabilized ICT state, whose formation occurs in 0.85–2.71 ps, depending on solvent. However, AF240 in nonpolar solvents and the symmetrical dyes in all solvents show essentially no shifts due to a predominantly locally excited (LE) state. Preliminary temperature-dependent fluorescence using frozen glass media supports significant solvent reorganization around the AF240 excited state in polar solvents, and may also support a twisted intramolecular charge-transfer (TICT)-state contribution to the stabilization. Finally, time-dependent density functional theory calculations support ICT in AF240 in polar media and also allow prediction of the 2PA cross sections in the 0–0 band, which are much larger for AF240 than the symmetrical dyes.					
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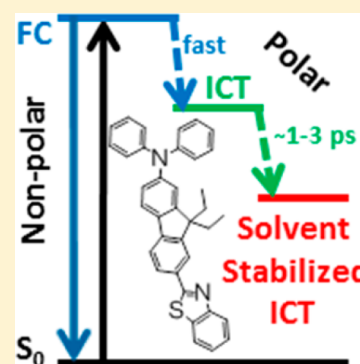
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Symmetry- and Solvent-Dependent Photophysics of Fluorenes Containing Donor and Acceptor Groups

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ABSTRACT: Three two-photon absorption (2PA) dyes (donor- π -donor (DPA2F), donor- π -acceptor (AF240), and acceptor- π -acceptor (BT2F); specifically, D is Ph₂N-, A is 2-benzothiazoyl, and the π -linker is 9,9-diethylfluorene) are examined in a variety of aprotic solvents. Because the 2PA cross section is sensitive to the polarity of the local environment, this report examines the solvent-dependent linear photophysics of the dyes, which are important to understand before probing more complex solid-state systems. The symmetrical dyes show little solvent dependence; however, AF240 has significant solvatochromism observed in the fluorescence spectra and lifetimes and also the transient absorption spectra. A 114 nm bathochromic shift is observed in the fluorescence maximum when going from *n*-hexane to acetonitrile, whereas the lifetimes increase from 1.25 to 3.12 ns. The excited-state dipole moment for AF240 is found to be 20.1 D using the Lippert equation, with smaller values observed for the symmetrical dyes. Additionally, the femtosecond transient absorption (TA) spectra at time zero show little solvent dependence for DPA2F or BT2F, but AF240 shows a 52 nm hypsochromic shift from *n*-hexane to acetonitrile. Coupled with the solvatochromism in the fluorescence and large excited-state dipole moment, this is attributed to formation of an intramolecular charge-transfer (ICT) state in polar solvents. By 10 ps in AF240, the maximum TA in acetonitrile has shifted 30 nm, providing direct evidence of a solvent-stabilized ICT state, whose formation occurs in 0.85–2.71 ps, depending on solvent. However, AF240 in nonpolar solvents and the symmetrical dyes in all solvents show essentially no shifts due to a predominantly locally excited (LE) state. Preliminary temperature-dependent fluorescence using frozen glass media supports significant solvent reorganization around the AF240 excited state in polar solvents, and may also support a twisted intramolecular charge-transfer (TICT)-state contribution to the stabilization. Finally, time-dependent density functional theory calculations support ICT in AF240 in polar media and also allow prediction of the 2PA cross sections in the 0–0 band, which are much larger for AF240 than the symmetrical dyes.



INTRODUCTION

Two-photon absorption (2PA) is defined as the electronic excitation of a molecule induced by a simultaneous absorption of a pair of photons and has become widely used in areas such as microscopy,^{1,2} microfabrication,³ nonlinear absorption,⁴ and photodynamic therapy.⁵ The sensitivity of a two-photon absorber is determined by its 2PA cross section, σ_2 , which is controlled by the molecular structure⁶ and also the surrounding media.⁷ Therefore, an understanding of the structure–property relationships is important in the design of 2PA molecules. It has been shown that intramolecular charge-transfer (ICT) processes can significantly enhance 2PA.^{8–13} Thus, both the permanent ground-state and excited-state dipole moments and the transition dipole moment are considered key parameters in the 2PA process.¹⁴ This necessitates design of molecules with electron-donating (D) and/or electron-accepting (A) groups or increasing the π -conjugation length.^{15–18} One particular class of compounds that has received significant attention in this area is fluorene-bridged derivatives.^{19–25} These molecules are often

designed as either symmetrical (D- π -D or A- π -A) or asymmetric (D- π -A) with the fluorene serving as the π -bridge. A number of functional donors (such as dimethylamino, diphenylamino, carbazoles, pyrroles, and dialkylamino) and acceptors (such as ketone, nitro, pyridine, and benzothiazole) have been explored.^{6,26,27}

Because the effective σ_2 is also sensitive to the polarity of the local environment,^{7,28} our report examines the solvent-dependent structure–property photophysical relationships of three of these molecules: 7-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-*N,N*-diphenyl-9H-fluorene-2-amine (AF240, D- π -A type), 9,9-diethyl-*N,N,N',N'*-tetraphenyl-9H-fluorene-2,7-diamine (DPA2F, D- π -D type), and 2,2'-(9,9-diethyl-9H-fluorene-2,7-diyl)dibenzo[*d*]thiazole (BT2F, A- π -A type) (Figure 1). These dyes have been studied previously in our group in spin-

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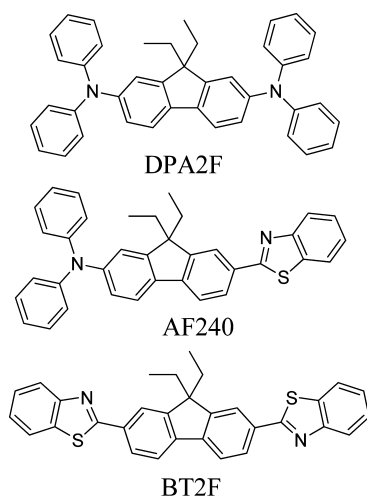


Figure 1. Structures of the dyes.

cast films blended with bisphthalimides for exciplex formation.^{29,30} Solvent-dependent studies by Belfield et al. on similar dyes³¹ and BT2F³² revealed strong solvatochromism on the emission spectra of D- π -A derivatives, but little dependence in symmetrical molecules. They also showed that a solvent-stabilized state is formed in the asymmetrical fluorene but showed no direct evidence of this process. Here we expand on these studies by including additional solvents, temperature-dependent emission, ground- and excited-state dipole calculations, and femto- and nanosecond transient absorption. Additionally, in terms of excited-state absorption (ESA), the importance of this study is evident as the cascaded one-photon absorption from an excited state may create an additional contribution to the nonlinear effects (a 2PA-assisted ESA).^{6,33} Therefore, tuning of the ESA energy via polarity changes in the surrounding media may play an important role in 2PA.

Models can often help elucidate the relationship between linear properties and σ_2 . Generally, for most organic chromophores, the 2PA and cross sections can be described with a few states model (FSM) derived by a sum-over-states approach because there are only a few important excited states involved in the optical transitions. For a simple dipolar, asymmetric chromophore a two-level model is often sufficient and a three-level model is useful for symmetric, quadrupolar dyes. Symmetry considerations are important for the identification of which excited states are most active in the 2PA process; selection rules dictate that the S1 state is most prevalent for dipolar chromophores and the S2 is most active for quadrupolar. For the two level model σ_2 is proportional to the square of the transition dipole moment ($|\mu_{01}|^2$) and the square of the permanent dipole moment difference between ground and excited state ($|\Delta\mu_{01}|^2$). For the three-level model for the symmetric chromophore, the permanent dipole moments go to zero, and σ_2 is proportional to the square of the transition dipole moments, $|\mu_{01}|$ and $|\mu_{12}|$. In short, factors that change the dipole moment affect σ_2 , and the interested reader is referred to the literature for a more detailed quantitative treatment of the FSM and 2PA cross section if interested.^{34–36}

EXPERIMENTAL SECTION

Instrumentation. NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer, and chemical shifts

were referenced to the solvent residual peak. Elemental analyses and mass spectral analyses were performed at Systems Support Branch, Materials & Manufacturing Directorate, Air Force Research Lab, Dayton, OH.

Ground-state UV/vis absorption spectra were measured on a Cary 500 spectrophotometer. Emission spectra were measured using a Cary Eclipse fluorometer, with 375 nm excitation for all samples. Time-correlated single-photon counting (Edinburgh Instruments OB 920 Spectrometer) was utilized to determine excited-state lifetimes. The sample was pumped using a 70 ps laser diode at 375 nm. Emission was detected on a cooled microchannel plate PMT. Data were analyzed using a reconvolution software package provided by Edinburgh Instruments. Fluorescence quantum yields were determined using the actinometry method previously described.³⁷ Quinine sulfate was used as an actinometer with a known fluorescence quantum yield of 0.54 in 0.5 M H₂SO₄.³⁸ All experiments were performed at room temperature. Temperature-dependent fluorescence spectra and lifetimes were obtained using an Oxford Instruments OptistatDN2 cryostat.

Nanosecond transient absorption measurements were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 8 mJ cm⁻² at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus has been published earlier;³⁷ however, a Princeton PI-MAX:1K was used as the detection source in lieu of the photomultiplier tube. All samples were freeze-pump-thaw degassed prior to use. Ultrafast transient absorption measurements were performed using a modified version of the femtosecond pump-probe UV-vis spectrometer described elsewhere.³⁹ Briefly, 1 mJ, 150 fs pulses at 800 nm at 1 kHz repetition rate were obtained from a diode-pumped, Ti:sapphire regenerative amplifier (Spectra Physics Hurricane). The output laser beam was split into pump and probe (85 and 15%) by a beam splitter. The pump beam was directed into a frequency doubler (CSK Super Tripler) and then was focused into the sample. The probe beam was delayed in a computer-controlled optical delay (Newport MM4000 250 mm linear positioning stage) and then focused into a sapphire plate to generate white light continuum. The white light was then overlapped with the pump beam in a 2 mm quartz cuvette and then coupled into a CCD detector (Ocean Optics S2000 UV-vis). Data acquisition was controlled by software developed by Ultrafast Systems LLC.

Computation. To model the excited-state properties of these systems, we used the Gaussian 09 suite of programs.⁴⁰ Solvent effects were calculated by the polarizable continuum model (PCM) method. Excited-state properties were calculated using linear response time-dependent density functional theory (TDDFT-PCM).⁴¹ These calculation methods gave non-equilibrium ground-state excitation energies and the corresponding relaxed excited-state solvent emission energies. Ground- and excited-state dipole moments were calculated by standard population analysis procedures yielding the correct analytical derivatives of the energy.⁴²

Materials and Methods. The syntheses of AF240,²⁰ DPA2F,^{30,43} and BT2F²³ have been previously reported. Quinine sulfate was purchased from Lancaster Synthesis. All solvents were of spectroscopic grade, purchased from Aldrich or Fisher, and used without further purification. Other than the nanosecond transient absorption, all other experiments were performed with air-saturated samples.

RESULTS AND DISCUSSION

Figure 1 shows the structures of the three dyes. The ground-state absorption spectra in varying solvents are shown in Figure 2, and relevant properties are listed in Table 1. The spectra are

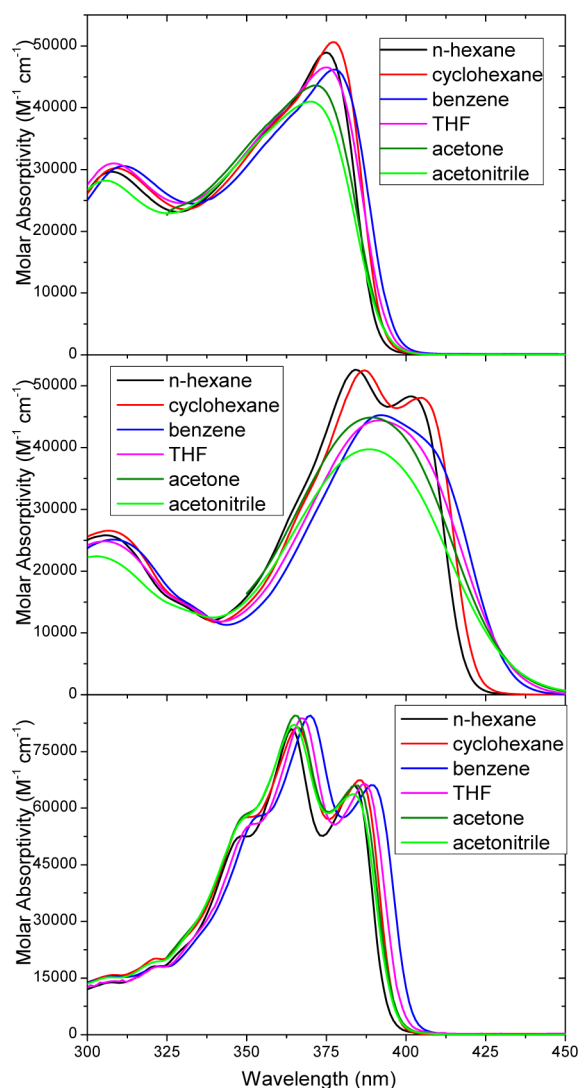


Figure 2. Ground-state absorption spectra of DPA2F (a), AF240 (b), and BT2F (c) in various solvents.

characterized by $\pi \rightarrow \pi^*$ transitions in the 350–400 nm range, consistent with other AFX dyes.⁴⁴ There is a slight general blue shift in DPA2F with increasing polarity, whereas almost no change is observed for BT2F. The slight broadening of the DPA2F spectra with increasing polarity indicates a small amount of ground-state ICT. However, these are minimal changes and the transition is still to a largely, locally excited (LE) state. As no changes in spectral shape or wavelength are observed in BT2F with changing solvent polarity, it is assigned as purely LE absorption.

AF240 exhibits much different behavior than the symmetrical dyes. As solvent polarity increases, there is significant broadening and loss of structure in the absorption spectra. The changes in maxima are minimal and show no trends with solvent. The broadening supports an appreciable amount of ground-state ICT in AF240. However, this transition is still from a largely LE ground state as no major shifts in wavelength

are observed.¹⁶ One important note is that the spectra for all three dyes in benzene are slightly red-shifted relative to the other solvents. This is attributed to stabilization of the π^* level via interaction of the benzene π system with that of the dyes.

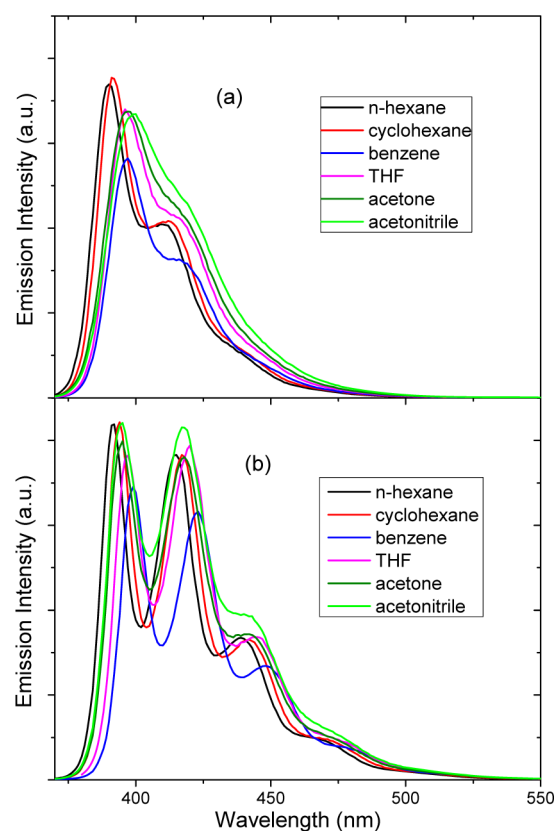
The emission spectra of DPA2F and BT2F are shown in Figure 3 and relevant properties listed in Table 1. Both dyes have structured spectra in all solvents with DPA2F being more broad. The emission spectra of DPA2F also show larger shifts and broadening with increasing solvent polarity than BT2F. The fluorescence quantum yields and lifetimes are essentially independent of solvent for BT2F, with a slight general increase in both values observed for DPA2F. Additionally, the radiative rate constants are unchanged for BT2F but show a slight decrease with increasing solvent polarity for DPA2F. These results are consistent with the absorption data. The small changes in all measurements over a wide range of solvent polarities suggest the S_1 state is largely LE in nature. However, DPA2F does contain an ICT state whose contribution, albeit small, is dependent on the solvent polarity. As with the absorption spectra, slight red shifts are observed in benzene which are attributed to stabilization of the lowest unoccupied molecular orbital (LUMO) by π – π interactions between the solvent and solute.

The D– π –A nature of AF240 produces a much different effect as significant solvatochromism is observed. The fluorescence spectra (Figure 4 and Table 1) are structured and high energy in nonpolar solvents but begin to broaden and red-shift considerably as the polarity increases. A 114 nm bathochromic shift in the maximum is observed from *n*-hexane to CH_3CN ($\epsilon = 1.89$ to $\epsilon = 37.5$). This supports a conversion from an LE to ICT state dependent on the solvent-controlled reaction coordinate. The quantum yields show a considerable decrease with increasing solvent polarity, while the lifetimes increase. This is in contrast to previous work, in which no trend was observed for an AF240-like molecule that only differs in the length of alkyl chains on the fluorene.³¹ Due to our observed trend and repeatability of the experiment, we are confident in our values. The lifetimes, however, were very similar for the solvents that were the same. The decrease in the quantum yield with increasing polarity is attributable to a decrease in the radiative rate constant while the nonradiative rate constant remains relatively stable (Table 1). Because the LE and ICT states are distinctly different, so too are their intrinsic properties. The LE state has a fast radiative rate constant that leads to the high quantum yields in nonpolar solvents. The ICT state has a much slower radiative rate constant—likely caused by greater charge separation and potential excited-state twisting (discussed below)—which allows internal conversion to compete and decreases the quantum yield.

Preliminary temperature-dependent emission data are shown in Figure 5. AF240 was examined in xylenes and a 4:5 propionitrile:butyronitrile mixture. Fluorescence spectra were measured at 300 and 100 K in each solvent, which both formed a transparent glass at 100 K. In the relatively nonpolar xylenes, the fluid and frozen spectra are comparable in energy, with only slight changes in the vibronic structure induced by the inhibited molecular motion when frozen. However, in the polar nitriles, a 53 nm hypsochromic shift is observed going from fluid to frozen. Additionally, the frozen spectrum becomes slightly structured. The dramatic difference in the nitriles is caused by the inability of the solvent to reorganize to stabilize the dipole formed in the ICT state. The state observed when frozen is likely a mixture of LE and ICT states. Although restricted

Table 1. Photophysical Properties of Dyes in Various Solvents^a

	solvent	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Stokes shift/ cm^{-1}	Φ_{em}	τ/ns	$k_t/10^8 \text{ s}^{-1}$	$k_{\text{nr}}/10^8 \text{ s}^{-1}$
AF240	<i>n</i> -hexane	384	52700(2200)	417	2046	0.68(0.03)	1.25(0.06)	5.4(0.5)	2.6(0.2)
	cyclohexane	387	52200(600)	419	2015	0.74(0.02)	1.43(0.07)	5.2(0.4)	1.8(0.1)
	benzene	392	45700(700)	443	2972	0.72(0.01)	1.61(0.08)	4.5(0.3)	1.7(0.1)
	THF	391	44400(2200)	475	4748	0.61(0.03)	2.12(0.11)	2.9(0.3)	1.8(0.2)
	acetone	389	44600(300)	503	6228	0.55(0.04)	2.65(0.13)	2.1(0.3)	1.7(0.2)
	acetonitrile	389	40200(700)	533	7122	0.42(0.03)	3.12(0.16)	1.3(0.2)	1.9(0.2)
DPA2F	<i>n</i> -hexane	375	48900(600)	390	1048	0.46(0.03)	0.88(0.04)	5.3(0.6)	6.1(0.7)
	cyclohexane	377	50700(2200)	392	975	0.54(0.04)	0.94(0.05)	5.5(0.7)	5.2(0.7)
	benzene	377	46200(500)	397	1280	0.50(0.04)	1.03(0.05)	4.8(0.6)	4.9(0.6)
	THF	375	46500(900)	396	1430	0.50(0.04)	1.03(0.05)	4.8(0.6)	4.9(0.6)
	acetone	372	43600(800)	397	1783	0.53(0.04)	1.13(0.06)	4.7(0.6)	4.2(0.5)
	acetonitrile	370	41000(1200)	399	1990	0.55(0.04)	1.23(0.06)	4.5(0.5)	3.6(0.4)
BT2F	<i>n</i> -hexane	364	80900(700)	392	526	0.77(0.05)	0.74(0.04)	10.4(1.3)	3.1(0.4)
	cyclohexane	366	81500(3900)	394	543	0.74(0.05)	0.75(0.04)	9.9(1.2)	3.4(0.4)
	benzene	370	84600(5600)	399	611	0.73(0.05)	0.71(0.04)	10.3(1.3)	3.7(0.5)
	THF	367	83800(2600)	397	645	0.73(0.05)	0.77(0.04)	9.5(1.2)	3.5(0.4)
	acetone	365	84500(500)	395	684	0.74(0.05)	0.78(0.04)	9.6(1.2)	3.3(0.4)
	acetonitrile	365	82000(500)	395	759	0.80(0.06)	0.80(0.04)	10.0(1.2)	2.5(0.3)

^aError indicated in parentheses.Figure 3. Steady-state emission spectra of DPA2F (a) and BT2F (b) in various solvents, $\lambda_{\text{ex}} = 375 \text{ nm}$.

solvent motion is one cause for the observed changes from fluid to frozen, the inability of AF240 to twist in the excited state may also affect the stabilization. The results suggest molecules in the LE state may remain in a geometry similar to that of the ground state whereas those in the ICT state stabilize by forming a twisted intramolecular charge-transfer (TICT) state. More work examining excited-state twisting is underway on

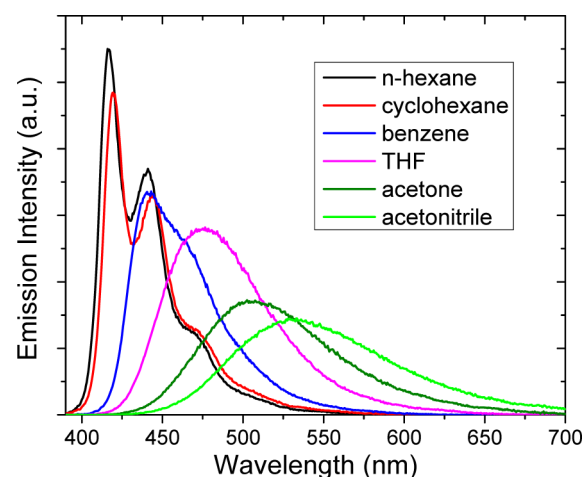
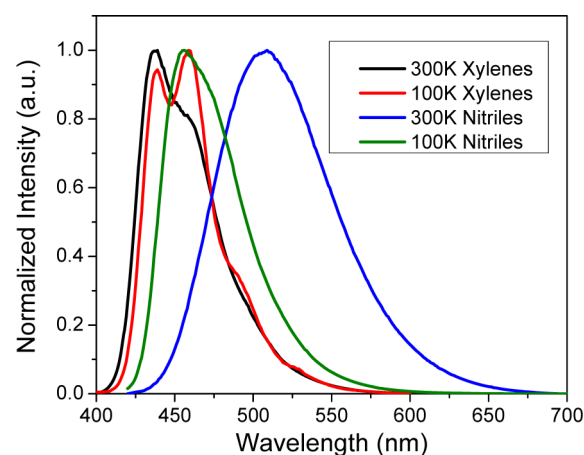
Figure 4. Steady-state emission spectra of AF240 in various solvents, $\lambda_{\text{ex}} = 375 \text{ nm}$.

Figure 5. Temperature-dependent emission spectra of AF240 in xylenes and 4:5 propionitrile:butyronitrile.

these and similar sterically hindered dyes to further our understanding of its effects on the photophysical properties.

To elaborate on the solvatochromism of the dyes we employ the Lippert–Mataga relationship (eq 1) where $\Delta\nu$ is the Stokes shift, $\Delta\mu_{ss}$ is the effective molecular dipole moment difference between the excited state and ground state, h is Planck's constant, c is the speed of light, and a is the radius of the solute spherical cavity. The Onsager radii, a , were determined by the molecular volume calculated by Gaussian.

$$\Delta\nu = \frac{2\Delta\mu_{ss}^2 \Delta f}{hca^3} + \text{constant} \quad (1)$$

Δf is the solvent polarity parameter determined from eq 2, where ϵ is the dielectric constant and n is the refractive index of the solvent.

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

A plot of Stokes shift versus the solvent polarity parameter for all three dyes is shown in Figure 6. The Onsager radii used

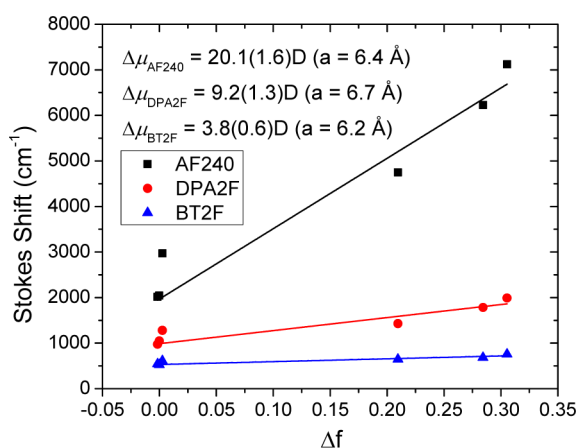


Figure 6. Lippert–Mataga plot for AF240, DPA2F, and BT2F.

for the determination of $\Delta\mu_{ss}$ are embedded in the plot. The results give $\Delta\mu_{ss}$ values of 20.1, 9.2, and 3.8 D for AF240, DPA2F, and BT2F, respectively. These data support the above conclusions of ICT contribution increasing with BT2F < DPA2F < AF240. It should be noted that the data points for benzene for each solvent were excluded from the fits because of their abnormally red-shifted emission. When only the other five solvents are considered, the data are still not perfectly linear, especially for AF240. This indicates there are solvent–solute effects separate from just polarizability. The cause is likely 2-fold. First, the nature of the emitting state is not consistent across all solvents as it changes from LE to ICT (or a mixture), especially in AF240 and to some extent, DPA2F. Second, the preliminary temperature-dependent data on AF240 suggests excited-state twisting could occur following photoexcitation and ICT. Therefore, the Stokes shift is attributed not only to

solvatochromism but also to the changing nature of the emitting state and potential stabilization of the excited state via twisting.

Calculations of the dipole moments of the ground (μ_{00}), transition (μ_{01}), Franck–Condon (FC, μ_{11}), and solvent optimized (SO, μ_{SO}) states are shown in Table 2 and support the experimental data. The calculations were performed using heptane and acetonitrile as solvents. The ground-state dipole moments show only small changes (≤ 0.20) when going from heptane to acetonitrile, consistent with the minimal changes in absorption maxima for all dyes. However, the value for AF240 is approximately twice as large as the other two dyes, which supports the broadening of the ground-state absorption spectra. DPA2F and BT2F show only modest changes in their excited-state dipole moments when compared to those of the ground state. The values for BT2F actually decrease for both the FC and SO states, although these changes are quite small. DPA2F does show a slight increase for both the FC and SO states relative to the ground state, and the values are noticeably larger in acetonitrile. These data support the larger solvent dependence on the excited state of DPA2F relative to BT2F. However, the SO value is nearly the same as the FC for both dyes, showing there is not significant solvent reorganization following excitation. As expected, major differences are observed when the excited-state dipole moments of AF240 are compared with those of the symmetrical dyes. The dipole moment of the FC excited state of AF240 is at least 10 times larger than that of DPA2F and BT2F in both solvents. There is a slightly larger FC dipole moment observed for AF240 in CH₃CN compared with that in heptane due to some ground state ICT, discussed above. Once the SO state is formed, the excited-state dipole moment increases by 1.26 in heptane and 5.53 in acetonitrile. This supports significant solvent reorganization, especially in polar solvents, and a solvent-stabilized excited state.

The previously discussed calculated ground-state, excited-state, and transition dipole moments allow for estimation of the far-off resonance 2PA cross section, σ_2 , of the lowest energy transition (0–0) using eq 3:^{45,46}

$$\sigma_2 = \frac{2(2\pi)^4 f_{\text{opt}}^4}{15(nch)^2} |\mu_{01}|^2 |\Delta\mu_{01}|^2 (2\cos^2\theta + 1)g(2\nu_L) \quad (3)$$

where $\Delta\mu_{01}$ is the difference of permanent electric dipole moments between the ground and the excited state ($\mu_{11} - \mu_{00}$), θ is the angle between the two vectors, ν_L is the laser frequency, f_{opt} is the optical local field factor, n is the refractive index, c is the velocity of light in vacuum, and $g(2\nu_L)$ is the line shape function (Hz^{−1}), normalized according to

$$\int g(x) dx = 1 \quad (4)$$

In linear-shaped molecules such as those studied here, the transition dipole moment vector and the permanent dipole

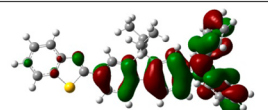
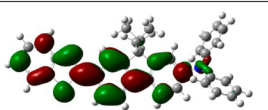
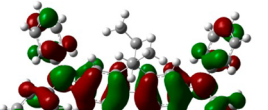
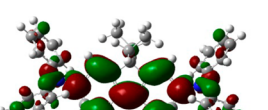
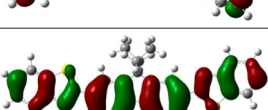
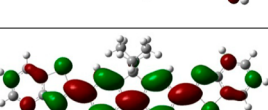
Table 2. Calculated Dipole Moments for the Ground (μ_{00}), Transition (μ_{01}), Franck–Condon (μ_{11}), and Solvent Optimized (μ_{SO}) States as Well as the Maximum Two-Photon Cross Section ($\sigma_{2,\text{calc}}$) for the 0–0 Band

dye	heptane					acetonitrile				
	μ_{00}	μ_{01}	μ_{11}	μ_{SO}	$\sigma_{2,\text{calc}}$ (GM)	μ_{00}	μ_{01}	μ_{11}	μ_{SO}	$\sigma_{2,\text{calc}}$ (GM)
AF240	1.19	4.13	11.61	12.87	417	1.31	4.58	13.30	18.73	641
DPA2F	0.52	3.70	1.01	0.74	0.74	0.68	4.04	1.24	1.12	1.09
BT2F	0.68	4.81	0.61	0.58	0.026	0.88	4.78	0.73	0.72	0.11

moment vector both tend to align parallel to the long axis of the molecule, so θ is assumed to equal 0. It is also assumed the local field factor is $f_{\text{opt}} = (2 + n^2)/3$. The results (Table 2) predict significantly larger σ_2 (given in GM, $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$) in the 0–0 band for AF240, with a higher value in CH_3CN than in heptane. The symmetrical dyes show only modest increases going from heptane to CH_3CN . The results indicate much better instantaneous 2PA response in the 0–0 band for dipolar AF240 than the symmetrical dyes, with tunability dependent on solvent polarity. However, we note that the cross section of the symmetrical dyes will be significant at higher energies when an intermediate state (S_1) can provide resonant enhancement (we are not able to calculate μ_{12} for the symmetric dyes and provide an assessment of max 2PA cross-section using a 3-level model because there are large number of higher excited states with similar energies).

Molecular orbital diagrams of the dyes (Table 3) obtained from TDDFT calculations further support our findings. The

Table 3. Molecular Orbital Diagrams for AF240, DPA2F, and BT2F

	HOMO	LUMO
AF240		
DPA2F		
BT2F		

highest occupied molecular orbital (HOMO) of AF240 contains electron density largely localized on the diphenylamino and fluorene groups. In contrast, the LUMO has the majority of its electron density on the benzothiazole and fluorene. This accounts for the large difference between the ground and excited state dipole moments and supports the observed ICT state. The other two dyes show much smaller changes from HOMO to LUMO. DPA2F does show some electron density transfer from the phenyl groups onto the fluorene, whereas BT2F shows very minimal changes. These data support the larger $\Delta\mu$ observed for DPA2F relative to BT2F.

Femtosecond transient absorption spectra for DPA2F and BT2F are shown in Figures 7 and 8, respectively, and their relevant properties listed in Table 4. At time zero (Figure 7a), S_1-S_n spectra for DPA2F are observed with two maxima centered near 520 and 600 nm. There is a marginal hypsochromic shift in both peaks with increasing solvent polarity, which is consistent with the small solvatochromism observed in the emission spectra. Here, the S_1 state is slightly stabilized in more polar solvents while the upper states remain relatively unaffected, leading to higher energy S_1-S_n transitions. BT2F (Figure 8a) shows even less solvent dependence, as expected due to its smaller excited state dipole. It has only one major peak near 685 nm with a much smaller peak at shorter

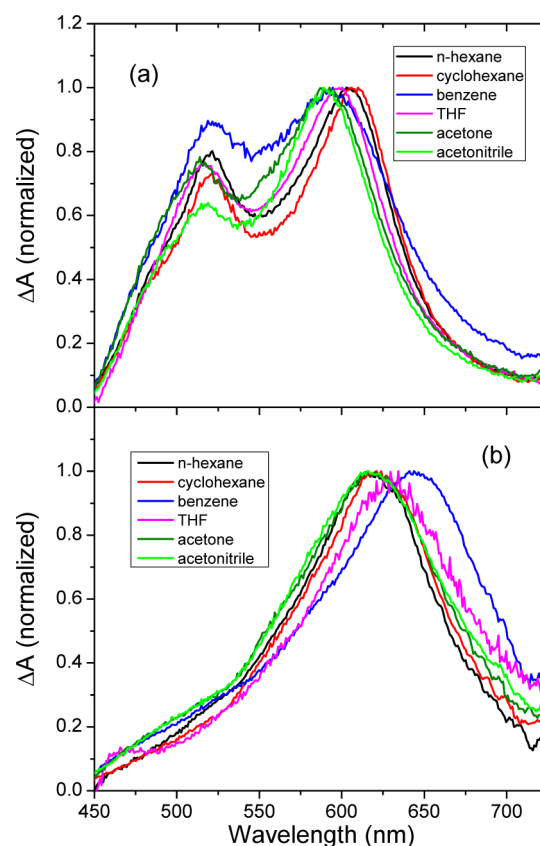


Figure 7. Femtosecond transient absorption spectra of DPA2F in various solvents at time zero (a) and time = 6 ns (b). Spectra in (b) correspond perfectly to the ns TA spectra.

wavelength. Single exponential fits were used to analyze the decay of both dyes (Table 4). The lifetimes are very similar to those observed by TCSPC and correspond to the fluorescence decay.

As the S_1-S_n transitions decay, T_1-T_n transitions appear in all solvents for DPA2F and BT2F (Figures 7b and 8b). For brevity, only the data at 6 ns from the femtosecond experiment are shown as they overlay perfectly with those from the nanosecond experiment. The spectra and table show these are also very solvent independent. However, as with the absorption and emission data, there is a noticeable red shift in the maxima for benzene. In the triplet manifold, the T_n state is stabilized more than the T_1 , lowering the T_1-T_n energy gap and leading to the lower energy maxima observed in benzene. The lifetimes were fit to either single or double exponentials. The results show no consistent trends, other than most being double-exponential and having a long lifetime greater than 100 μs , consistent with the forbidden spin-flip required to return to the ground state. All were run with the same absorbance at the excitation wavelength, eliminating self-quenching processes as an explanation.

The transient absorption properties of dipolar AF240 are markedly different than the other two dyes. The normalized spectra at time zero are shown in Figure 9a. The broad spectra show a large solvent dependence as a significant hypsochromic shift is observed with increasing polarity. The negative ΔA signals are due to fluorescence. The S_1 state is stabilized in polar solvents so the transitions to upper states become higher in energy as polarity increases. The results indicate that significant ICT has already occurred in the more polar solvents within the

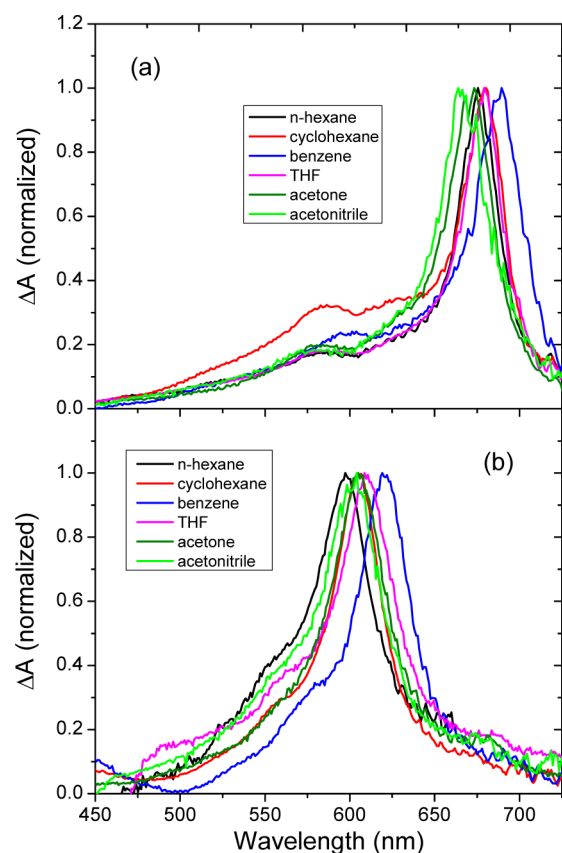


Figure 8. Femtosecond transient absorption spectra of BT2F in various solvents at time zero (a) and time = 6 ns (b). Spectra in (b) correspond perfectly to the ns TA spectra.

instrument response time (a few hundred femtoseconds). By 10 ps (Figure 9b) even larger shifts have occurred, whose

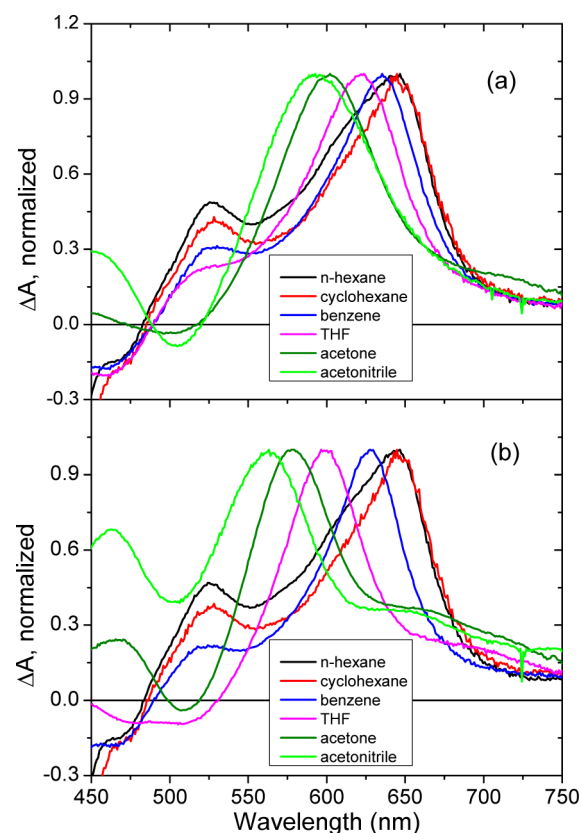


Figure 9. Femtosecond transient absorption spectra of AF240 at time zero (a) and time = 10 ps (b).

magnitudes increase with increasing polarity. For example, the maximum in benzene shifts only seven nm from time zero to 10 ps, whereas that for CH_3CN shifts 30 nm. The nonpolar solvents *n*-hexane and cyclohexane have essentially no shifts

Table 4. Transient Absorption Properties of Dyes in Various Solvents^a

solvent		femtosecond					nanosecond	
		$\lambda_{\text{max}}/\text{nm } t = 0 \text{ ps}$	$\lambda_{\text{max}}/\text{nm } t = 10 \text{ ps}$	$\lambda_{\text{max}}/\text{nm } t = 6 \text{ ns}$	τ_1/ps	τ_2/ps	$\lambda_{\text{max}}/\text{nm}$	$\tau_1/\mu\text{s}$
AF240	<i>n</i> -hexane	644	645	678		1010(270)	688	84(1)
	cyclohexane	645	646	709		1160(60)	698	316(16)
	benzene	635	628		2.71(1.09)	1210(240)		
	THF	622	601		2.38(2.13)	1940(110)		
	acetone	602	578		0.85(0.30)	2190(170)		
	acetonitrile	592	562		0.96(0.32)	2800(250)		
solvent		femtosecond				nanosecond		
		$\lambda_{\text{max}}/\text{nm } t = 0 \text{ ps}$	$\lambda_{\text{max}}/\text{nm } t = 10 \text{ ps}$	$\lambda_{\text{max}}/\text{nm } t = 6 \text{ ns}$	τ_1/ps	$\lambda_{\text{max}}/\text{nm}$	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$
DPA2F	<i>n</i> -hexane	604/522	604/521	618	1310(130)	615	18.5(1.0)	
	cyclohexane	606/521	608/521	619	940(30)	623		122(5)
	benzene	593/520	592/521	643	980(30)	642	41.0(2.7)	213(12)
	THF	598/517	599/517	629	1620(370)	626	26.6(4.4)	161(14)
	acetone	590/515	589/515	619	1350(120)	622	37.1(1.9)	242(11)
	acetonitrile	590/518	589/516	617	1210(60)	614	3.66(0.61)	29.6(1.2)
BT2F	<i>n</i> -hexane	685	685	598	691(26)	597		118(4)
	cyclohexane	688	688	605	735(17)	603	2.17(0.01)	
	benzene	695	696	620	755(16)	620	38.5(3.0)	218(10)
	THF	688	687	609	766(35)	610	79.6(5.7)	510(113)
	acetone	681	681	605	895(37)	603	46.1(1.8)	256(14)
	acetonitrile	676	677	603	818(11)	601	50.5(1.6)	259(11)

^aError indicated in parentheses.

during this time frame. These data indicate a solvent-stabilized ICT (SSICT) state forming in the four most polar solvents, which is supported by the calculations mentioned previously.

Lifetimes for this process are given in Table 4 and show a general trend of decreasing with increasing polarity, as the more polar solvents can more rapidly stabilize the ICT state. The lifetimes range from 0.85–2.71 ps, which is plausible for solvent reorganization.^{15,47} On the basis of the temperature-dependent emission data, this stabilization likely includes excited-state twisting. Although the longer lifetimes are slightly shorter than those observed by TCSPC, they follow the same polarity trend and are considered to be due to decay of the S_1 state.

The nanosecond transient absorption experiment only showed measurable triplet signals for AF240 in *n*-hexane and cyclohexane (Figure 10), which had maxima at 688 and 698 nm

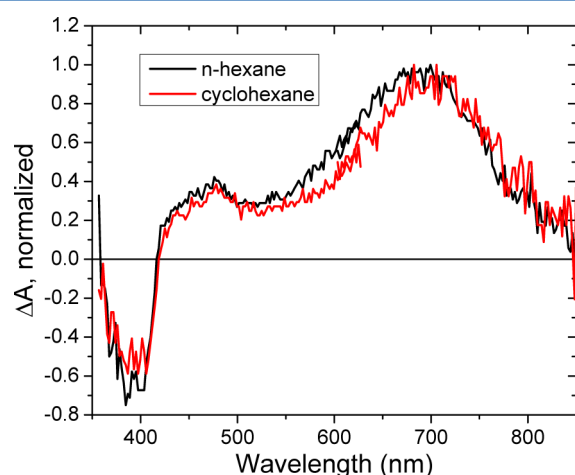


Figure 10. Nanosecond transient absorption spectra of AF240 in *n*-hexane and cyclohexane.

and lifetimes of 84 and 316 μ s, respectively. Considering their similar polarities, the discrepancy in the values is still puzzling. Other noticeable features in the spectra include a higher energy

T_1 – T_n transition near 470 nm and the bleach of the ground state absorption near 400 nm. Because ICT contributes to the S_1 state in the other solvents, the quantum yield for triplet formation decreases significantly, and triplet signals are not observed. There is precedence for this in the literature.⁴⁸ Additionally, if excited-state twisting is indeed occurring the ICT triplet can be higher than the singlet, preventing intersystem crossing (ISC).⁴⁹ Our group did previously observe a triplet signal for AF240 in THF.^{50,51} However, that experiment was done using a more sensitive detector and the signal was still very weak. Though intersystem crossing is not completely eliminated from the ICT singlet state, we can state with certainty it is greatly reduced relative to the LE state.

The overall results are summarized in Figure 11. The left diagram shows the processes involved in the symmetrical dyes and AF240 in nonpolar solvents. Ground-state absorption occurs to the singlet LE(FC) state. Following absorption, the excited state can decay via fluorescence or internal conversion, absorb a photon to a higher-lying singlet state, or undergo ISC to form the triplet. Here, the ICT state (not shown) lies higher in energy than the LE, preventing ICT formation. Because this process is eliminated, the localized triplet can form, and it is observed under these conditions. When AF240 is in polar solvents, four pathways are possible following absorption: internal conversion to the ground state, fluorescence via radiative decay, excited-state absorption, or formation of an ICT state. Rapid ICT formation occurs within a few hundred femtoseconds, as the first observable transient is already significantly shifted. Next, solvent reorganization occurs with a time constant of 850–2710 fs, depending on solvent, to yield the SSICT state. The energy of this state is highly solvent dependent, decreasing with increasing polarity. This state decays via fluorescence and internal conversion, with very minimal to no triplet formation.

CONCLUSIONS

We have measured absorption, fluorescence spectra, lifetimes, quantum yields, and transient absorption for three 2PA fluorene derivatives in a number of aprotic solvents. The

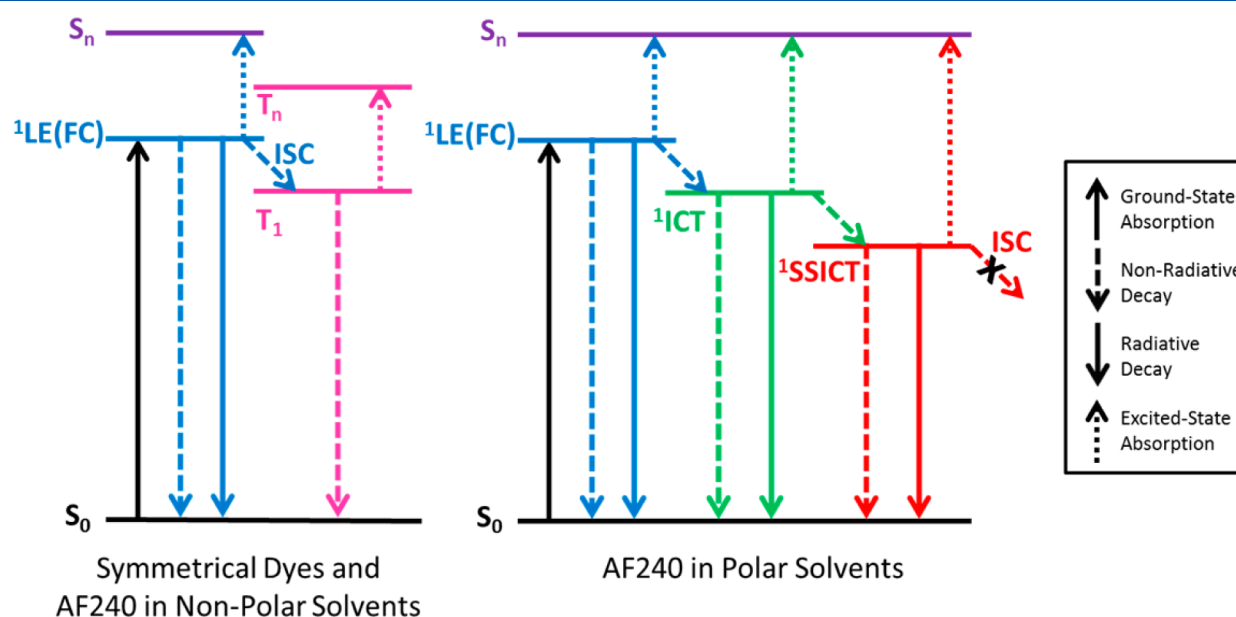


Figure 11. Diagram showing the solvent-dependent photophysical processes.

results show significant solvatochromism on the fluorescence and transient absorption spectra for the asymmetric dye (AF240), but little dependence on the symmetrical molecules (DPA2F and BT2F). Excited-state dipole moments determined by experiment and calculations were also observed to be much larger for AF240, consistent with the solvatochromism observed. Femtosecond transient absorption allowed observation of the solvent relaxation around AF240 in the four most polar solvents. This relaxation occurred on a time scale of 0.85–2.71 ps and was faster in more polar media. This gives direct evidence of a solvent-stabilized excited state. Additionally, for AF240, the ESA maximum was very dependent on solvent. This provides tunability of the ESA when an ICT state is present and suggests guidelines for selecting proper media environment to obtain desired ESA and potentially increase effective 2PA. Also, a simple two-level model suggests that the instantaneous 2PA cross section of dipolar chromophores increases as a function of solvent polarity. Solvent-dependent 2PA measurements are currently underway in both the nano- and femtosecond regime. Early temperature-dependent results suggest solvent reorganization and potentially a TICT state are critical in stabilization of AF240 in polar media. The amount of stabilization that can occur by twisting becomes an important consideration if 2PA dyes are ultimately doped or incorporated in motion-restricting solid media.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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